



SEQUENTIAL PROCESSING REACTION VESSEL FOR CHEMICAL FRACTIONATION AND ANALYSIS

CROSS-REFERENCES

5 This application is related to co-pending U.S. provisional patent application U.S.S.N. 60/177,837 filed on January 25, 2000 which is incorporated herein by this reference.

FIELD OF THE INVENTION

This invention relates to devices and methods for sequential fractionation and extraction of elements from complex solid samples . More particularly, this invention relates to a
10 sequential processing reaction vessel and method for accelerated fractionation and extraction of analytes from solid samples which is compatible with microwave heating sources and which reduces processing time and transfer losses, improves extraction efficiency, and provides for accurate total analysis of solid samples.

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BACKGROUND OF THE INVENTION

Sequential extraction methods have been previously developed to address specific questions to enhance understanding of elemental behavior in complex oceanographic and geological samples [see R. Chester et al., *Chemical Geology*, 2: 249-262 (1967); A. Tessler et al., *Analytical Chemistry*, 51(7): 844-850 (1979); D. W. Eggemann et al., *Jour. Sediment Petrol.* 50: 215-225 (1980); J. M. Robbins et al., "A Sequential Extraction Procedure for partitioning elements among co-existing phases in marine sediments", College of Oceanography, Oregon State University, Ref.#84-3, 64pp. (1984); S. B. Moran et al., *Geochimica Cosmochimica Acta*, 55: 2745-2751 (1991); and R. Chester et al., *Journal of the Geological Society, London*, 151: 351-360 (1994)].
20 Analytical techniques most commonly used for the chemical fractionation of Si in biogenic and lithogenic sedimentary particles are based on the higher solubility of biogenic silica in alkaline solutions at elevated temperature and pressure. Several variations of this technique require pretreatment of the sample, heating of the sample in the presence of an alkaline solution and the separation of the solution from the remaining particles [see D. W.
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Eggimann et al., *Jour. Sediment Petrol.* 50: 215-225 (1980); P. J. Muller et al., *Deep-sea Research*, Vol. 40, No. 3. Pp. 425-444 (1993); D. J. DeMaster, *Geophysical Monograph* 63: 363-367 (1991); and R. A. Mortlock et al., *Deep-sea Research*, Vol. 36, No. 9, pp. 1415-1426, (1989)].

5 Methods have been developed for the fractional analysis of marine sediment samples where the elements Ca, Mg, and Sr are associated with the biogenic carbonate fraction and lithogenic fraction [see M. Bender et al., *Micropaleontology*, vol. 21, no. 4, pp.448-459 (1975); and S. R. Taylor, *Geochimica et Cosmochimica Acta*, Vol. 28 pp.1273-1285 (1964)].

The separation of various chemical fractions of phosphorus is of particular interest to
10 biogeochemical researchers [see K. C. Ruttenberg, *Limnol. Oceanogr.*, 37(7), pp. 1460-1482 (1992)]. While fractionation methods have been developed for determining particulate phosphorus found in the water soluble and acid-soluble portion of ocean particles [see G. Liebezeit, *Marine Chemistry*, 33: 61-69 (1991)], the lithogenic P fraction has not yet been precisely characterized by existing methods.

15 The elements Al, Ti, and Fe that are primarily associated with the lithogenic component of ocean particles have a small but very significant fraction associated with biogenic material and adsorbed/scavenged elements. These fractions have been accessed by several chemical treatments [see K. W. Bruland et al., *Geochimica Cosmochimica Acta*, 58: 3171-3182 (1994); R. W. Murray et al., *Paleoceanography*, Vol. 8, No. 5, pp. 651-670 (1993); and
20 S. B. Moran et al., *Geochimica Cosmochimica Acta*, 55: 2745-2751 (1991)].

The current methods and reaction vessels for extracting elemental constituents from complex solid samples typically involve tedious, multi-stage solution treatments where solid samples must be repeatedly removed, weighed, dried and transferred between successive reaction vessels for extraction and fractionation analysis of individual constituents. Due to
25 repeated sample losses and contamination introduced during multiple sample transfers, such methods generally suffer from a lack of reproducibility, precision and accuracy. Due to the number of treatments and sample transfers typically required, such methods are intrinsically inefficient and due to the considerable sample preparation and transfer times.

It is anticipated that a method which could overcome the limitation of existing fractionation methods and substantially reduce sample transfers, preparation times and costs would be particularly beneficial to the analysis of solid samples in a variety of industrial, environmental and research applications.

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SUMMARY OF THE INVENTION

The sequential processing reaction vessel (SPRV) device and method of the present invention provide for accelerated sequential processing of solid samples at high temperatures and pressures within a single reaction vessel. The method employs a series of reagent 10 solution treatments introduced in a microwave transparent, flow-through reaction vessel that retains the solid samples on a membrane filter and frit while permitting introduction and removal of a variety of sample treatment solutions for extraction and fractionation analysis of target analytes.

The SPRV reactor is preferably fabricated with a microwave transparent 15 PTFEpolytetrafluoroethylene (PTFE) inner vessel and Ultempolyetherimide (sold under the trademark ULTEM®) outer vessel which permit microwave heating of the reactor for accelerated analyte extraction and sample digestion at temperatures up to 150° and pressures up to 150 psi.

The reactor of the present invention provides for rapid sample addition and removal by 20 providing for partial assembly of the reactor housing with retention of a sample membrane filter which facilitates charging of the reactor with solid samples prior to sequential processing solution treatments and eliminates sample transfer losses and contamination during addition of solids to the reactor. A variety of reagent solutions may be sequentially introduced and removed from the innovative reactor of the present invention without 25 disassembly or removal of the solid samples.

During operation of the device of the present invention, pressure can be introduced into the top cover opening to force liquid to pass out the bottom opening. This is an important featureand which permits automation of the flow-through system and allows the vessel and

sample to remain in the an oven while liquids can be programmed to flow in and out of the vessel. Additional auxiliary openings in the top cover permit the monitoring of reactor temperature and pressure during operation.

The device of the present invention further provides for an innovative laminated membrane filter for retention of solid samples during ~~sequential~~sequential processing treatment. The use of the innovative laminated filter provides for improved mechanical durability of the membrane when operating at high liquid pressures, eliminates liquid flow by-pass and leakage around the membrane, and maintains high solids retention while permitting pressurized fluid flow through the membrane when discharging reagent liquids at the end of treatment cycles.

The device and method of the present invention provide for efficient accelerated sequential processing of solid samples with a variety of reagent solutions for rapid, low cost fractionation analysis of solid materials with high analytical reproducibility, precision and accuracy and minimum sample losses or contamination due to unnecessary sample transfers.

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BRIEF DESCRIPTION OF THE DRAWINGS

This invention is pointed out with particularity in the appended claims. Other features and benefits of the invention can be more clearly understood with reference to the specification and the accompanying drawings in which:

Figs. 1A-1B are schematic diagrams of cross-sections of the sequential processing reaction vessel of the present invention in a sealed (Fig. 1A) and open (Fig. 1B) position;

Fig. 2 is a schematic diagram of the laminated membrane filter assembly of the present invention;

Fig. 3 is a schematic diagram of the liquid spray attachment for the SPRV of the present invention;

Figs. 4A-4C are schematic diagrams of an SPRV carousel assembly (Fig. 2A), top plate (Fig. 2B) (Fig. 4B) and bottom plate (Fig. 2C); (Fig. 4C); and

Fig. 5 shows sequentially extracted elemental concentrations in treatment solutions 1 through 9 for two marine sediment samples.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

1. Introduction

In recent years there has been an increasing demand to use sequential extraction methods to quantify elements in a vast number of ocean sediment and particle samples in 10 order to better understand biogeochemical processes, particularly for programs related to global change and paleoproxy research [see R. Chester et al., *Chemical Geology*, 2: 249-262 (1967); C. De La Rocha et al., *Analytical Chemistry*, 68: 3746-3750 (1996); S. Honjo et al., *Deep-Sea Research*, 40: 587-607 (1993); M. Lyle et al., *Geochimica Cosmochimica Acta*, 48: 1705-1715 (1984); R. W. Murray et al., *Paleoceanography*, Vol. 8, No. 5, pp. 651-670 15 (1993); and D. M. Nelson et al., *Global Biogeochemical Cycle*, 9, 359-372 (1995)]. One of the important examples of applications of a sequential extraction method is to distinguish concentrations of biogenic silicates (diatom frustules) from lithogenic silicates (clay minerals and structural silicates) in ocean sediment material.

When applying conventional extraction methods, sample throughput is constrained due 20 to the considerably slow reaction times and numerous time consuming sample transfers required with successive chemical treatments [see R. J. Collier et al., *Marine particles: Analysis and Characterization*, (ed.) D. C. Hurd et al., AGU Geophysical Monograph 63 (1991); D. W. Eggemann et al., *Jour. Sediment Petrol.* 50: 215-225 (1980)]. In order to overcome these limitations, an innovative sequential processing reaction vessel (SPRV) has 25 been developed that eliminates the typical sample transfer processes, losses and contamination encountered with conventional reactor devices and methods and substantially reduces sample processing time by facilitating rapid, sequential solution treatments and analyte fractionation and extraction from solid samples.

With the SPRV device and method of the present invention, a sample remains in a single reaction chamber throughout sequential reaction with a variety of chemical reagents. The SPRV device and method of the present inventions dramatically reduces the handling operations and processing time associated with conventional sequential extraction methods

5 which employ multiple sample transfers, centrifugations and filtrations. With the present SPRV device and method, sources of sample contamination and material losses, for example sample transfers, incomplete solids separation by centrifugation and sample removal from filters ~~is~~are eliminated. The device and method provide for rapid sequential treatment of solid samples with a variety of reagents over a range of reaction temperatures and pressures

10 which accelerate reaction and extraction of sample analytes. Solutions instantly reach the desired temperatures when they are heated in ~~the~~a microwave oven which accelerates reaction times. The heating rate, temperature, pressure, and time for sample treatments may be programmed with commercially available microwave ovens. Thus, the innovative device and method of the present invention significantly reduces the time required to extract

15 analytes and sequentially treat samples with a series of reagent solutions when compared to existing methods. For example, results from SPRV experiments show that the time required to dissolve biogenic Si from sediment sample PB123 in heated 1M Na₂CO₃ solution with the present device and method was reduced from 4 hours to 30 minutes.

20 2. SPRV Design

A schematic of the SPRV 100 is provided in Figs. 1A and 1B. As shown in Fig. 1A, the SPRV 100 comprises a top valve 105, a top securing collar 110, a top cover 115, a top cover O-ring 120, an exterior jacket 125, ~~an~~ interior liner 130, a membrane filter 135, a filter support frit 140, a filter holder 145, a filter holder o~~-~~ringring 150, a bottom securing ring 155, a bottom valve 160 and alignment pins 165. While Figs. 1A and 1B show only a single top valve 105, the top cover 115 may be equipped with additional auxiliary ports 116 for temperature or pressure probes used for measuring reaction chamber conditions. The interior volume formed by the top cover 115, interior liner 130 and filter holder 145 of the

SPRV is referred to herein as the reaction chamber. In one embodiment, the exterior dimensions of the ~~STRV~~SPRV 100 are 16cm high with a 6.5cm diameter and a reaction chamber volume of 50ml.

The SPRV 100 interior parts that come in direct contact with the sample and solutions
5 are preferably made of PFA (Teflon®) a perfluoroalkoxy-polytetrafluoroethylene copolymer material, sold under the trademark TEFLON® PFA, and all SPRV 100 exterior parts required for strength are preferably made of a polyetherimide material, sold under the trademark ULTEM®. Figs. 1A and 1B show one SPRV 100 embodiment where the interior parts, comprising a top valve 105, a top cover 115, an interior liner 130, a filter holder 145 and
10 bottom valve 160, are made of a polytetrafluoroethylene material, sold under the trademark TEFLON®, and the exterior parts, (Ultem®), comprising a top securing collar 110, an exterior jacket 125 and a bottom securing ring 155, are made of a glass-filled polyetherimide material, sold under the trademark ULTEM® 2300. Other materials may be employed as long as they are chemically resistant to treatment solutions and transparent to microwave
15 energy so that they may be used in a microwave oven. One innovative design feature of the SPRV 100 is the incorporation of the filter holder 145 within the housing of the SPRV 100. With this design, tightening of the bottom securing ring 155 threads on the exterior jacket 125 urges the filter holder 145 against interior liner 130 thereby compressing the filter holder O-ring 150 against the membrane filter 135 and housing members 130,135, interior
20 liner 130 and filter holder 145 and providing a leak-proof seal that withstands both the high temperatures and high pressures generated during operation of the SPRV 100.

While any suitable membrane filter 135 and filter frit support 140 materials may be employed, in preferred embodiments hydrophylic PTFE or Teflon®hydrophylic polytetrafluoro-ethylene, sold under the trademark TEFLON®, filters 135 and frit supports
25 140 are employed due to their wetting characteristics, chemical inertness and mechanical stability at high temperature and pressure. In alternative embodiments, hydrophobic PTFE may be employed as filters 135 and frit supports 140 providing the material is either pretreated with a wetting promoter solution or coated with a hydrophylic material. Testing of

PTFE filter materials showed that ~~this material~~they retained their integrity at reaction temperatures up to 150° C, reaction pressures up to 150 psi and at liquid flow pressures up to 30 psi. Other filter materials may be employed as long as they similarly possess these desirable properties. Where lower reaction temperatures are employed, alternative filter 135 and frit support 140 materials may be utilized. For example cellulosics, polyamides, acrylics, polyesters, styrenics, fluoropolymers, polyolefins or inorganics may be employed as alternative filter membrane 135 materials for lower temperature treatments. Similarly, high density polyethylene, ultra high molecular weight polyethylene, polypropylene, polyvinylidene fluoride, polystyrenes, ethylene vinyl acetate and polysulfone may be employed as alternative filter frit support 140 materials with lower temperature treatments.

While membrane filter 135 pore size may be selected based on either sample particulate size or digestion behavior, in preferred embodiments, membrane filters 135 having a pore size ranging from 0.45 to 3 microns are employed with particulate samples. In a preferred embodiment, a ~~hydrophylic, hydrophilic~~, PTFE, 0.5 um pore size, Millipore LCR Membrane Filter (Millipore Corp., Bedford, MA) is employed as the membrane filter 135 with perforated or porous 1/16 to 1/8 inch thick PTFE disk as a filter support frit 140. In the most preferred embodiment, an innovative laminated membrane filter 135 is employed which provides for improved filtration by eliminating fluid bypass and leakage around membrane filter edges, high solids retention by the 0.5 um LCR membrane filter, high fluid throughput through the 37 um PTFE filter, and enhanced mechanical strength for the fragile LCR membrane filter at fluid flow pressures up to 30 psi.

In this preferred laminated filter embodiment, a 0.5 um LCR Membrane Filter is first cut into a toroidal shape with a nominal 37 mm diameter and nominal ring width of 3 to 5 mm. This ring-shaped piece is then placed over a second 37 mm diameter, 0.5 um LCR Membrane Filter which is then placed over a 37 mm diameter, 37 um pore size PTFE filter. The outside perimeter of the three layers are then fused together by pressing the layers between two metal plates at 330° C for 15 minutes. This treatment produces a fused, bonded non-porous PTFE outer ring around the outside perimeter of an unbonded central area of the

LCR and 37 um filter and retains the 0.5 um pore size of LCR filter and the 37 um pore size of the PTFE filter. A schematic diagram of the laminated filter assembly is provided in Fig.

2. The resultant laminated membrane filter 135 is placed in the SPRV 100 with the LCR filter facing the top and the 37 um PTFE filter facing the bottom of the vessel 100.

5 The innovative laminated membrane filter of the present invention offers distinct advantages over conventional supported membrane filters which typically fuse a low pore size membrane filter to a coarser pore size support over the entire surface of the membrane. In these conventional supported membrane filters, the filtration pore size and performance of the membrane filter is typically compromised by the fusion treatment which typically bonds 10 the entire surface of the membrane filter to its support and generally results in undesirable pore blockage across the entire membrane filter-support interface leading to lower fluid permeability and higher pressure buildup across the membrane filter which leads to premature membrane rupture. With the innovative laminated membrane filter of the present invention, only limited area on the outside perimeter of the membrane is fused, leaving most 15 of the membrane filter surface and membrane support surface in ~~its~~their pristine state, thereby preventing pore blockage. Additionally, after fusion of the laminate, the fused ring on the outside perimeter forms a non-porous, compressible layer that extends beyond the filter holder o-ring 150 and compresses with the o-ring 150 during assembly of the SPRV 100 to form a tight, leak-proof seal which prevents undesirable liquid flow bypass and 20 leakage around membrane filter perimeter at high reactor or fluid pressures.

A cross section of the SPRV 100 configuration during sample loading is shown in Fig. 1B. By providing an independent means for securing the membrane filter ~~145~~135 with the bottom housing members 130, 145 and ~~O~~ringo-ring 150, the innovative SPRV 100 design enables removal of the top securing collar 110 and top cover 115 for immediate access to the 25 SPRV 100 reaction chamber for introduction of solid samples onto the membrane filter 135 through a large chamber opening at the top of the vessel. During operation the SPRV 100 is sealed (see Fig. 1A) and liquids can be introduced into the reaction chamber by opening the top valve 105 and removed from the chamber by opening the bottom valve 160. The top and

bottom valves 105, 160 thus provide for either continuous flow of liquid reactants through the chamber or the sequential addition of fluid reactants and extraction of analyte solutions during batch sample treatments without opening the vessel or removing and replacing samples. The valve cap openings 105, 160 at the top and bottom of the SPRV 100 enable
5 either pressure or vacuum to be applied to the reaction chamber to separate the liquid from sample solids retained on the filter 135. As shown if Figs. 1-2,1A and 1B, both the top 105 and bottom 160 valves incorporate a safety pressure relief seal 161 which ruptures in the event of excessive internal pressure during heating.

While the SPRV 100 may be heated with conventional convection or radiant heat
10 sources, in a preferred embodiment, the reaction vessel 100 is configured for heating in a microwave oven equipped ~~and equipped~~ with reaction chamber sensors for continuous monitoring of vessel 100 temperatures and pressures. In a preferred embodiment, the vessel 100 ~~was~~ is heated in a CEM MDS-2100 programmable microwave oven (CEM Corp., North Carolina). The MDS-2100 is equipped with an inboard pressure control system to monitor
15 and control pressure conditions inside the SPRV 100 reaction chamber. A pressure sensing line is fed through either the top valve 105 port or an auxiliary port on the top cover 115. Pressure is measured by a pressure transducer and displayed graphically and digitally on an LCD display. The MDS-2100 oven is also equipped with a fiber optic probe used to monitor and control SPRV reaction chamber temperature. A microwave transparent fiber
20 optic temperature probe is fed through either a top valve 105 port or an auxiliary port on the top cover 115. The temperature sensor is a phosphor which emits fluorescent light after excitation by an optical source. The decay rate of fluorescent emission is temperature dependent and provides for accurate and precise determination of the vessel 100 temperature. Details of the pressure and temperature sensor are provided in the MDS-2100
25 Operation Manual (CEM Corp., Matthews, NC, 1994)

3. SPRV Operation

In a typical operation of the SPRV 100, an approximately 10mg sample is introduced into the partially assembled reaction chamber (see Fig. 1B) through the top opening of the vessel. The top cover 115 and top valve 105 are then secured to the external and interior housing members 125, 130 with the top securing collar 110 (see Fig. 1A). With the bottom 5 valve 160 closed, approximately 10ml to 40ml of treatment solution is introduced into the reaction chamber by opening the top valve 105. The treatment solution can include any organic and inorganic reagents, acids, bases or solvents. The top valve 105 is closed and the sealed SPRV may then be heated by an external heat source up to 150° C. Due to the heating of the liquids to elevated temperatures in the enclosed reactor, pressures as high as 10 150 psi may be achieved. This combination of high reaction temperatures and pressures provide for accelerated reaction of the sample with treatment solutions. In one preferred embodiment, the vessel is heated at a rate of 1° to 2° C per minute to approximately 120° C at 40 to 50 psi and held at temperature for about 15 minutes. Other heating rates, reaction 15 temperatures and pressures may be readily employed by the skilled artisan based on the specific reagents used and sample reaction requirements. While conventional radiant heating or convection ovens may be employed for heating the SPRV 100, in a preferred embodiment the vessel and sample are microwave-heated in a programmable microwave oven. With this embodiment, rapid heating and cooling of the enclosed sample and reagents is achieved due to the microwave transparency of the SPRV 100 and microwave 20 absorbtionabsorption by the sample and reactants.

After reaction of the treatment solution with the sample at high temperature and pressure, the treatment solution ~~with~~containing extracted analytes ~~are~~is separated from the residual sample solids by the filter 135 and removed from the reaction chamber by draining the solution through the bottom valve 160. In a preferred embodiment, the fluid is 25 pressurized by introducing compressed nitrogen gas through the top valve 105 so as to force the liquid through the filter 135 and out of the chamber through the bottom valve 160. The filter 135 retains any remaining sample solids within the chamber for subsequent treatments. In a preferred embodiment, a laminated .5u PTFE membrane filter ~~was~~is employed due to its

inertness, strength, and ability to retain remaining fine particles. The chamber may be subsequently rinsed with the treatment solution, distilled water or solvent to flush any remaining reactants and extracted analytes from the reaction chamber.

Fig. 3 shows a schematic diagram of a liquid spray attachment 200 which is typically employed to either to add liquid reagents to the reaction chamber prior to a treatment cycle or to rinse the chamber at the end of a solution treatment. The spray attachment 200 comprises a spray tube 220 with one closed end inserted into the vessel 100 through the top valve port 105. The inserted tube 220 has a plurality of holes 230 machined along its length and perimeter. The tube 220 is connected to a liquid reservoir 210 which is filled with liquids through an entry cap 240. The cap 240 is equipped with a septum for injecting liquids with a syringe. A gas valve 250 is attached to the side of the reservoir 210 for introducing gas pressure to urge liquid in the reservoir 210 through the tube 220 and spray holes 230. The resultant liquid spray is uniformly distributed within the reaction chamber of the vessel 100 during filling and rinsing of the SPRV 100 before and after solution treatments. After rinsing of the vessel 100, additional solution or solvent may be added to the extracted liquid for adjusting analyte concentrations to a known volume. Typical analyte volumes range between 10 ml to 50 ml for treatments of 10 mg samples and the volume is adjusted ~~the adjust~~ to establish analyte concentration for optimum analysis using preferred analytical methods. The extracted solution and analytes may be directly analyzed by conventional spectrographic analytical methods. The entire process may be repeated for reacting additional alternative reagent solutions with the remaining sample solids according to desired sequential processing procedures which are selected for the sample and analytes of interest.

~~Table 1 lists the typical procedures employed in an SPRV solution treatment cycle.~~

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Table 1 SPRV Procedures.

1. Assemble the SPRV filter holder assembly according to Fig. 1B.

2. Figs. 1A and 1B show an example of an SPRV filter holder assembly. Typically, the bottom portion of the SPRV vessel 100, comprising the jacket 125, securing ring 155

and filter holder assembly, is initially assembled (see Fig. 1B). As shown in Figs. 1A and 1B, the membrane filter 135 is held in position by the o-ring 150, interior liner 130, filter holder 145 and alignment pins 165. If hydrophobic filters are used they must be "wetted" 135 are employed, they are wetted and rinsed with acetone or alcohol.

5 3.alcohol. Where vacuum is used, there is no need to secure the top valve cap 105. A vacuum of 200 mm of Hg is introduced in the SPRV vessel 100 by loosening the bottom valve For particle separation, either vacuum or pressure is used

10 4.If vacuum is used securing the top cap is not required The vessel is connected to a vacuum collecting vessel with tubing and a stopper through the SPRV bottom valve cap. The vacuum of 200mm Hg is introduced into the SPRV by rotating the bottom valve cap. The cap 160. As vacuum is applied, liquid is drawn through the vessel 100 and filter 135 and the filtrate is collected in the evacuated vessel.

5. If vessel 100. Where pressure is used the used, a top valve cap 105 must be attached.

Air pressure 30 psi is introduced by connecting the pressure tube to Both the top valve cap.

15 15 Both top 105 and bottom valve caps 160 valves must be open to filter the vessel contents. Typically, 30 psi air pressure is The filtrate is introduced through the top valve cap 105 and liquid is forced through the vessel 100 and filter 135 and collected in a container under the button valve cap bottom valve cap 160.

20 6.Rinse the filter with distilled H₂O. This removes the 'wetting solution and also reduces static which can be a problem Prior to sealing the SPRV vessel 100, the filter 135 is rinsed with distilled water to remove wetting solution and to reduce static problems when introducing samples into the vessel.

25 7.to the vessel 100. Approximately 10 mg of sample is weighed and placed at the bottom of the vessel on top of the filter 135 (see Fig. 1B). After securing the Weigh 10 mg of sample on a small weighing paper and with forceps carefully place it into the bottom of the vessel. (Fig 1B)

8.After securing top valve cap the SPRV is now ready for the top valve cap 105, the SPRV vessel 100 is ready for introduction of the solution treatment (Fig.1A).

30 9. Remove treatments. After removal of the top vent fitting and add the solution 161, solutions are added to the vessel 100 through the opening in the top valve cap.

10. Re-secure the cap 105. The vent fitting and follow 161 is secured and the procedures for the first solution treatment.

11.treatment is followed. If heating is required:

12.Use the required, a single opening valve cap 105 is used for conventional heating

35 13. Use the heating and a triple opening valve cap is used for microwave heating. The additional openings are required used with mircrowave heating are for monitoring temp and pressure

~~14. After heating the SPRV vessel 100 temperature and pressure. Following the heating treatment, the vessel 100 is cooled to room temperature prior to filtration. The contents can then be filtered according to step 3. filtrate is then withdrawn by either application of vacuum or pressure as noted above. For sequential treatments, additional solutions are introduced at the top valve 105 and the process is repeated for each treatment solution. An example treatment solution sequence is provided in Table 1.~~

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~~15. To sequentially treat the remaining sample with other treatment go to step 8~~

~~After the process is completed the entire treatment process is completed, the last treatment solution is separated from the remaining particles by draining it through the filter and the bottom valve, by introducing gas pressure from a pressurized source into the reaction chamber at the top valve 105 and draining the solution through the top valve filter 135 and collecting it from the bottom valve 160.~~

10 ~~treatment solution is separated from the remaining particles by draining it through the filter and the bottom valve, by introducing gas pressure from a pressurized source into the reaction chamber at the top valve 105 and draining the solution through the top valve filter 135 and collecting it from the bottom valve 160.~~

15 4. Multiple SPRV System

Sample throughput can be optimized by applying a multiple SPRV system to a large number of samples with the expectation of uniform results. The design and construction of a Multiple SPRV System enables processing a large number of samples simultaneously and results in a substantial reduction in processing time and costs compared to existing sample preparation methods. The Multiple SPRV System consists of a plurality of SPRV units (Fig. 1A) arranged on carousel assemblies (~~Figs. 4A-C~~).300 (see Figs. 4A-4C). In one embodiment, a Multiple SPRV System for processing 20 samples simultaneously may be employed. In alternative embodiments, the number of SPRV units 100 and carousels 300 may be varied to meet heating oven requirements. By increasing sample throughput, a Multiple SPRV System provides for significantly improvements in time and cost of elemental analysis of sediment, slurry or particulate samples while improving accuracy, precision, and reliability of analytical results when compared to existing procedures.

20 ~~units (Fig. 1A) arranged on carousel assemblies (Figs. 4A-C).300 (see Figs. 4A-4C). In one embodiment, a Multiple SPRV System for processing 20 samples simultaneously may be employed. In alternative embodiments, the number of SPRV units 100 and carousels 300 may be varied to meet heating oven requirements. By increasing sample throughput, a~~

25 ~~Multiple SPRV System provides for significantly improvements in time and cost of elemental analysis of sediment, slurry or particulate samples while improving accuracy, precision, and reliability of analytical results when compared to existing procedures.~~

As shown in Fig. 4B-4C, the carousel 300 is typically machined from UHMW polyethylene to accommodate a plurality of SPRV reactors 100. In one embodiment, the

carousel comprises a support ~~pedastal~~pedestal 310, which is configured to mount on a rotating ~~pedastal~~pedestal mount 305 of a microwave oven 301. A carousel bottom plate 320 is attached to the support ~~pedastal~~pedestal 310 with a series of bolts 355~~345~~ (not shown) passing through the botom plate bolt holes 350. The carousel top plate 330 is similarly

5 attached to the support pedestal 310 with a series of bolts 345 (not shown) passing through the top plate 330 bolt holes 340. The carousel bottom plate 320 is machined with a plurality openings configured to register with the SPRV bottom valve assembly 160. The ~~carousle~~carousel top plate 330 is machined with a plurality of openings configured to register with the SPRV exterior jacket assembly 125. In one embodiment, each SPRV

10 carousel assembly 300 holds ten SPRVs 100 and is designed to attach to the rotating ~~pedistal~~pedestal of a programable microwave oven (see Fig.4C).Fig.4A). In alternative embodiments, both the number of SPRVs per carousel and the number of carousels employed can be varied and their respective dimensions may be adapted to conform to the interior dimension of the microwave oven. During microwave heating the SPRV carousel is

15 alternately rotated clock-wise and counterclock-wise 360 degrees so that microwave heating is uniform for all the SPRV vessels. The carousels and SPRVs are easily removed and interchange so that while one multiple SPRV-carousel assembly is being processed, unmounted SPRV-SPRV-carousel assemblies can be prepared off-line for the next treatment cycle.

20 To evaluate the Multiple SPRV System, a variety of ~~testsolution~~treatment methods and conditions, as noted in the section below, may be applied to selected reference samples. For example, a combination of four separate solution treatments may be employed which include acidic and alkaline solution treatments as well as elevated ~~temperatures and pressure~~temperature and pressure treatments on sediment reference materials of well known

25 composition. The Multiple SPRV System permits simultaneous testing of various sediment reference materials during complex sequential chemical treatments. The multiple station device provides for replicate samples and reagent blanks to be simultaneous processed with a series of complex sequential treatments to determine the analytical precision of elemental

analysis during multi-sample processing. Known total elemental analysis on sample reference materials enables mass balances to be calculated for each sample to monitor the complete recovery of partitioned elements.

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5. Sequential Extraction Methods

Sequential extraction methods have been developed to address specific questions to enhance for enhanced understanding of elemental behavior in complex oceanographic and geological samples [see R. Chester et al., *Chemical Geology*, 2: 249-262 (1967); A. Tessler 10 et al., *Analytical Chemistry*, 51(7): 844-850 (1979); D. W. Eggemann et al., *Jour. Sediment Petrol.* 50: 215-225 (1980); J. M. Robbins et al., "A Sequential Extraction Procedure for partitioning elements among co-existing phases in marine sediments", College of Oceanography, Oregon State University, Ref.#84-3, 64pp. (1984); S. B. Moran et al., *Geochimica Cosmochimica Acta*, 55: 2745-2751 (1991); and R. Chester et al., *Journal of the Geological Society, London*, 151: 351-360 (1994)]. While numerous reaction methods and treatments may be combined in varying sequences to develop sequential processing methods for specific sample types and target analytes in a variety of geological, marine, environmental, research and industrial applications, four example sequential processing and fractionation methods are provided below as typical example applications for which the 15 20 SPRV device and method of the present invention are particularly suitable.

Method 1: Techniques most commonly used for the chemical fractionation of Si in biogenic and lithogenic sedimentary particles are based on the higher solubility of biogenic silica in alkaline solutions at elevated temperature and pressure. Several variations of this technique require pretreatment of the sample, heating of the sample in the presence of an 25 alkaline solution and the separation of the solution from the remaining particles [see D. W. Eggemann et al., *Jour. Sediment Petrol.* 50: 215-225 (1980); P. J. Muller et al., *Deep-sea Research*, Vol. 40, No. 3. Pp. 425-444 (1993); D. J. DeMaster, *Geophysical Monograph* 63: 363-367 (1991); and R. A. Mortlock et al., *Deep-sea Research*, Vol. 36, No. 9, pp. 1415-

1426, (1989)]. It is anticipated that the SPRV device and method of the present invention will radically simplify the complex and lengthy procedures of the existing methods and substantially reduce reaction time for dissolving the biogenic Si in alkaline solutions.

Method 2: In marine sediment samples the elements Ca, Mg, and Sr are associated with
5 the biogenic carbonate fraction and lithogenic fraction [see M. Bender et al.,
Micropaleontology, vol. 21, no. 4, pp.448-459 (1975); and S. R. Taylor, *Geochimica et Cosmochimica Acta*, Vol. 28 pp.1273-1285 (1964)]. Since these elements are also major constituents of seawater, significant analytical corrections are required if removal of seawater from the solids is incomplete [see R. J. Collier et al., *Marine particles: Analysis*
10 *and Characterization*, (ed.) D. C. Hurd et al., AGU Geophysical Monograph 63 (1991)]. It is anticipated that the SPRV device and method of the present invention will allow effective pretreatment of the sediment to remove seawater prior to analysis, thereby eliminating the need for sea-salt corrections [see M. Lyle et al., *Geochimica Cosmochimica Acta*, 48: 1705-1715 (1984)]. It is anticipated that innovative treatments removing the carbonates from the
15 lithogenic fraction in these samples may be possible with the SPRV device and method.

Method 3: The separation of various chemical fractions of phosphorus is of particular interest to biogeochemical researchers [see K. C. Ruttenberg, *Limnol. Oceanogr.*, 37(7), pp. 1460-1482 (1992)]. . Particulate phosphorus is found in the water soluble and acid-soluble portion of ocean particles [see G. Liebezeit, *Marine Chemistry*, 33: 61-69 (1991)] while the
20 lithogenic P fraction has not yet been precisely characterized by existing methods. It is anticipated that the SPRV device and method of the present invention will facilitate chemical fractionation of these multiple forms of phosphorus due to the improved chemical partitioning methods offered.

Method 4: The elements Al, Ti, and Fe that are primarily associated with the lithogenic
25 component of ocean particles have a small but very significant fraction associated with biogenic material and adsorbed/scavenged elements. These fractions have been accessed by several chemical treatments [see K. W. Bruland et al., *Geochimica Cosmochimica Acta*, 58:

3171-3182 (1994); R. W. Murray et al., *Paleoceanography*, Vol. 8, No. 5, pp. 651-670 (1993); and S. B. Moran et al., *Geochimica Cosmochimica Acta*, 55: 2745-2751 (1991)]. It is anticipated that precise sequential chemical treatments and fractionation can be achieved with the SPRV device and method of the present invention. Additionally, the complete
5 dissolution of the most resistant solid phases may be achieved by adapting Totland's method [see Totland et al., *Chemical Geology*, 95: 35-62 (1992)] and employing strong acids and microwave heating with the SPRV device of the present invention.

While the SPRV device and method may be applied to any one of the tedious analytical determinations described above in realizing significant cost and time savings over the
10 existing methods, the SPRV device and method uniquely provides for combining all four analytical methods for sequential processing of samples within a single reaction vessel to provide elemental fractionation, extraction and analysis of complex sample chemical constituents with both a substantial savings in processing time and expense as well as a corresponding improvement in analytical accuracy and reproducibility due to elimination of
15 transfer losses and contamination.

EXAMPLE 1

Two ocean sediment reference materials of different component composition were treated in the SPRV with four treatment solutions at elevated temperatures and pressures.
20 They two ocean sediment reference materials were marine particulate samples collected by a sediment trap in the Panama Basin (PB123) consisting primarily of biogenic components (i.e. carbonate, biogenic silicate and organic components) and a deep ocean surface sediment sample from the Southern Ocean (PC40) consisting primarily of lithogenic particles (i.e. clay minerals and structural silicates). Replicates of four samples were processed for each
25 sample type. For these samples , a total of nine sequential treatments were employed, including: a) two distilled H₂O treatments at room temperature; b) two treatments of 1N acetic acid at room temperature; c) four treatments of 1M Na₂CO₃ at elevated temperatures

90°C, 120° C, 150 C, and 150 °C; and one treatment of HNO₃/HF at 150 °C. Details of the sequential treatments are provided in Table 2-1.

The treatment solutions of Table 2-1 were chosen because they extract elements associated with the major components of ocean sediment material. The elements associated with water soluble and sea water component are expected to be predominantly in treatment solutions 1 and 2. The elements associated with the carbonate component are expected to be predominantly in treatment solutions 3 and 4 treated with 1M acetic acid. The elements associated with the biogenic silicate component with minor contributions from the lithogenic component are expected to be predominantly in treatment solutions 5 –8. The elements of the remaining lithogenic component are expected to be completely dissolved by the HNO₃/HF treatment and contained in treatment solution 9. Major and minor elements for each sample solution, including Ca, Mg, Sr, Si, and Al, were analyzed by ICP-ES. The analytical results for each treatment solution utilized with the two samples are provided in Fig.5.

Results from the elemental concentrations in the nine treatment solutions and microscopic examination of the filters indicate that all particulate material was removed from the ~~filter~~ filter by the nine sequential treatments. As shown in Fig. 5, the elements associated with the major components of oceans sediments were extracted into the expected treatment solutions. For example, with the PB123 sample, high concentrations of Si were detected in 1M Na₂CO₃ solutions 5-7 indicating the biogenic silicate component. Furthermore, with this sample high concentrations of Ca, Mg and Sr, representing the carbonate component, were detected in the in acetic acid solutions 3 and 4 . In contrast, with the PC40 sample, the majority of elements were detected in solution 9, indicating dissolution of the resistant lithogenic component by the HNO₃/HF treatment. While sequential extraction techniques may have limitations regarding interpretation of element extraction behavior due to sample composition and element chemical properties [see J. M. Martin et al., *Marine Chemistry*, 22: 313-341 (1987); and C. Kheboian et al., *Analytical Chemistry*, 59: 1417-1423 (1987)], as the results shown in Fig. 5 demonstrate, the unique advantages

and efficiencies of the SPRV reactor and its associated processing methods have been clearly demonstrated its use as an invaluable tool for fractionating elements in solid samples and providing total analysis of solid samples with high reproducibility and accuracy.

5

EXAMPLE 2

A series of SPRV tests were performed to compare conventional convective heating with microwave heating when dissolving biogenic Si in heated alkaline treatment solutions. The chemical fractionation of biogenic and lithogenic sedimentary particles was conducted based on the higher solubility of biogenic silica in alkaline solutions at elevated temperature
10 and pressure. Three reference samples containing biogenic Si as the primary component were utilized to evaluate the efficiency of alternative alkaline solution treatments: a) sediment trap diatoms with some radiolarians (AE-2-3); b) core sample radiolarians with traces of diatoms (JB rads); and c) core sample diatoms with some radiolarians (P26).

Approximately 5 to 10 mg of sample was placed in the SPRV reaction chamber with 10
15 ml of 1 M Na₂CO₃ and heated (a) with a conventional convection oven, with shaking every 30 min, at constant temperatures of 90° C, 120° C and 150° C for four hours, and (b) with a microwave oven programmed for 10 minute heating at 90° C, 120° C and 150° C. After treatment, samples were examined under a light microscope to determine the presence or absence of biogenic particles. The test results indicate that biogenic Si in sediment trap
20 reference material (AE-2-3) dissolved after four hours treatment in a conventional oven at 90° C as anticipated while microwave heating dissolved the sample in 10 minutes at 120° C. The biogenic Si in reference core materials (Jb rads and PC26) were never completely dissolved with four hours heating at 120° in the conventional oven but were completely dissolved in 10 minutes heating at 120°C with microwave heating.

25

Table 2.1. Treatment Solution Sequence

| Treatment Solutions | Vol. — (ml) | Temp. (°C) | Time (min.) | Elements associated with treatment solutions |
|---------------------------------------|-------------|------------|-------------|--|
| TREATMENT SOLUTIONS | Vol. (ml) | Temp. (°C) | Time (min.) | ELEMENTS ASSOCIATED WITH TREATMENT SOLUTIONS |
| 1) distilled H ₂ O | 10 | 22 | 30 | Elements associated with the water soluble and sea water component |
| 2) distilled H ₂ O | 10 | 22 | 30 | |
| 1) distilled H ₂ O | 10 | 22 | 30 | Elements associated with the water soluble and sea water component |
| 2) distilled H ₂ O | 10 | 22 | 30 | |
| 3) 1N acetic acid | 10 | 22 | 30 | Elements associated with the acid soluble and carbonate component |
| 4) 1N acetic acid | 10 | 22 | 30 | |
| 3) 1N acetic acid | 10 | 22 | 30 | Elements associated with the acid soluble and carbonate component |
| 4) 1N acetic acid | 10 | 22 | 30 | |
| 5) 1M Na ₂ CO ₃ | 10 | 90 | 10 | Elements associated with biogenic silicate component, (diatom and radiolarian tests), and lithogenic component |
| 6) 1M Na ₂ CO ₃ | 10 | 120 | 10 | |

| | | | | |
|---|-----------|------------|-----------|---|
| 5) <u>1M Na₂CO₃</u> | <u>10</u> | <u>90</u> | <u>10</u> | <u>Elements associated with biogenic silicate component, (diatom and radiolarian tests), and lithogenic component</u> |
| 6) <u>1M Na₂CO₃</u> | <u>10</u> | <u>120</u> | <u>10</u> | |
| 7) <u>1M Na₂CO₃</u> | <u>10</u> | <u>150</u> | <u>10</u> | <u>Elements associated with the robust biogenic silicate component and lithogenic component</u> |
| 8) <u>1M Na₂CO₃</u> | <u>10</u> | <u>150</u> | <u>10</u> | |
| 7) <u>1M Na₂CO₃</u> | <u>10</u> | <u>150</u> | <u>10</u> | <u>Elements associated with the robust biogenic silicate component and lithogenic component</u> |
| 8) <u>1M Na₂CO₃</u> | <u>10</u> | <u>150</u> | <u>10</u> | |
| 9) 98% HNO ₃ +2% HF | 5 | 150 | 15 | Elements associated with the remaining resistant and lithogenic component |

Having described the preferred embodiments of the invention, it will now become apparent to one of skill in the art that other embodiments incorporating the disclosed concepts may be used. Therefore, it is not intended to limit the invention to the disclosed embodiments but rather the invention should be limited only by the spirit and scope of the following claims.

~~SEQUENTIAL PROCESSING REACTION VESSEL FOR CHEMICAL FRACTIONATION AND ANALYSIS~~

ABSTRACT

5

A sequential processing reactor vessel and method is disclosed for accelerated extraction and fractionation of chemical analytes from complex solid sample materials. The device and method provide for sequential extraction of elemental constituents from solid materials by sequentially contacting target samples within a single reaction vessel using a series of different reagents at temperatures as high as 150° C and pressures up to 150 psi to accelerate reactions. The aggressive chemical treatments provided by the disclosed device and method ~~provide for enable~~ the complete digestion of solid samples in liquid analyte samples that can be directly analyzed by conventional spectrometry or other suitable methods. The disclosed device and method provide for efficient sample processing and accelerated reactions to significantly reduce processing times and costs for elemental analysis of solids while improving accuracy, precision and reliability of results compared to conventional devices and methods. The disclosed device and method are compatible with both conventional convection and radiant heating sources as well as microwave heating and can be readily adapted to marine, geological, environmental, industrial and research solids analysis applications.